UTILIZATION OF RICE STRAW IN THE PRODUCTION OF SOME CELLULOSIC DERIVATIVES

Submitted By Hany Aly El Sayed El Germ

B.Sc. of Science (Botany/Chemistry), Faculty of Science, Ain Shams University, 1998
 Diploma in Environmental Sciences, Institute of Environmental Studies and Research,

 Ain Shams University, 2002

 Master in Environmental Sciences, Institute of Environmental Studies and Research,

 Ain Shams University, 2010

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Doctor of Philosophy Degree
In
Environmental Sciences

Department of Environmental Basic Sciences Institute of Environmental Studies and Research Ain Shams University

APPROVAL SHEET

UTILIZATION OF RICE STRAW IN THE

PRODUCTION OF SOME CELLULOSIC DERIVATIVES

Submitted By Hany Aly El Sayed El Germ

B.Sc. of Science (Botany/Chemistry), Faculty of Science, Ain Shams University, 1998 Diploma in Environmental Sciences, Institute of Environmental Studies and Research, Ain Shams University, 2002

Master in Environmental Sciences, Institute of Environmental Studies and Research, Ain Shams University, 2010

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Doctor of Philosophy Degree

In

Environmental Sciences
Department of Environmental Basic Sciences

This Thesis Towards a Doctor of Philosophy Degree in Environmental Sciences Has been Approved by:

Name

Signature

1- Prof. Dr. Mostafa Mohamed Hassan Khalil

Prof. of Inorganic and Analytical Chemistry Faculty of Science Ain Shams University

2- Prof. Dr. Mona Abd El-Kader Nassar

Prof. and Head of Department of Packaging National Research Center

3- Prof. Dr. Taha Abd El Azzem Mohamed Abd El-Razek

Prof. of Environmental Analytical Chemistry
Vice Dean of Institute of Environmental Studies & Research for
Environment & Community Affairs
Ain Shams University

4- Prof. Dr. Maha Mohamed Ahmed Ibrahim

Prof. of Cellulose and Paper National Research Center

2018

UTILIZATION OF RICE STRAW IN THE PRODUCTION OF SOME CELLULOSIC DERIVATIVES

Submitted By Hany Aly El Sayed El Germ

B.Sc. of Science (Botany/Chemistry), Faculty of Science, Ain Shams University, 1998
 Diploma in Environmental Sciences, Institute of Environmental Studies and Research,
 Ain Shams University, 2002

Master in Environmental Sciences, Institute of Environmental Studies and Research,

Ain Shams University, 2010

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Doctor of Philosophy Degree

In

Environmental Sciences
Department of Environmental Basic Sciences

Under The Supervision of:

1- Prof. Dr. Ashraf Ahmed Hamed

Prof. of Organic Chemistry Faculty of Science Ain Shams University

2- Prof. Dr. Maha Mohamed Ahmed Ibrahim

Prof. of Cellulose and Paper National Research Center

3- Dr. Taha Abd El Azzem Mohamed Abd El-Razek

Associate Prof. of Environmental Analytical Chemistry Head of Department of Environmental Basic Sciences Institute of Environmental Studies Ain Shams University

Acknowledgment

I would like to thank Prof. Dr. Ashraf A. Hamed, Professor of Organic Chemistry, Faculty of Science-Ain Shams University, for his encouragement and support.

I would like to thank Prof. Dr. Maha M. Ibrahim, Professor of Cellulose and Paper, National Research Center, for her outstanding effort, encouraging, guiding and supervision.

I would like to thank Dr. Taha Abdel Azim Mohamed A. Razek, Assistant Prof. of Environmental Chemistry, Department of Basic Science – Environmental Studies and Research Institute, for the great effort he did and the fruitful advise he gave.

Finally, my hearty thanks to my family who constantly encouraged me to go forwards.....

Abstract

Egypt produces around 4 million tons of rice straw / annually. Fields must be cleaned from straw to make way for the next crop. Soil incorporation and field burning have been the major practice for removing rice straw. Field burning damage the land by killing useful microorganisms in the soil and incorporation in the soil is slower, more expensive and may promote rice diseases. The smoke from the rice straw combustions is also a potential health hazard for humans because it could give rise to asthma and cancer. Cellulosic compounds are the most important renewable natural resources on earth. Cellulose is the main component of plant cell walls, and the basic building block for many textiles and for paper. Cellulose is a hard crystalline material fibrous enough to use as paper, textiles, clothes, strings, sanitary goods, etc.. Cellulose is insoluble in water and most common solvents. Bonding between the individual chains prevents it from being broken by mild chemicals or water, and makes it resistant to enzyme decomposition. Hydrogen bonds, which give cellulose stability, are broken down through pretreatment methods by chemical reactions that take place in hydroxyl groups and glucosidic linkage of cellulose molecule. Cellulose has the ability to functionalize chemically to provide cellulose derivatives, such as cellulose esters and ethers which have important applications in our daily life such as in textiles, pharmaceuticals, food, and packaging industries. It is directly linked to the paper industry. Cellulose derivatives are further used as coatings, laminations, optical films and absorbents. Ionic liquids (IL) possess not only a high chemical and thermal stability, nonflammability and a negligible vapor pressure, but also the recycling of these solvents is comparably easy. Recently, certain ILs have been applied as green solvents which would dissolve cellulose and function as inert and homogeneous reaction media, found that the ionic liquids containing Cl⁻ have excellent capability to dissolve cellulose e.g.1-butyl-3-methylimidazolium chloride (BMIM)+Cl-. Cellulose solutions with up

to 25 wt% cellulose can be prepared using 1-butyl-3 methylimlidazolium chloride under microwave heating. Cellulose is precipitated easily using methanol, water or ethanol and the regenerated cellulose is rarely degraded and has polymerization degree and polydisperity that is close to the initial cellulose.

In an attempt to take advantage of agricultural waste such as rice straw, which causes an environmental problem, it was used as a cellulose source with ionic liquid, which can be recovered after the reaction, into cellulose derivatives such as methyl cellulose, carboxymethyl cellulose and hydrogel preparation of derivatives. Derivatives and hydrogels were used as additives to the pulp during the paper preparation process with other additives. The mechanical and optical properties of the resulting paper were studied. The experiments showed an improvement in the mechanical and optical properties of the resulting paper. The study showed that the water absorption rate in the paper was increased with the addition of both MC and CMC to reach 230 and 290%, respectively. On the other hand, addition of both MC-hydrogel and CMC-hydrogel produces absorbed paper with water uptake till 773 and 600%, respectively which means obtaining high absorbent paper.

Keywords: Rice straw – Ionic Liquid – Cellulose Derivatives

List of Contents

Title	Page No.
List of Figures	V
List of Tables	VII
List of Abbreviations	VIII
List of Symbols	IX
Chapter 1- Introduction	
1-1- General	1
- Aim of The Work	4
Chapter 2- Literature Review	
2-1-Rice Straw	6
2-1-1- Rice Production in Egypt	8
2-1-2- Amount of Rice Straw	8
2-1-3- Rice straw Burning	9
2-1-4-Emmissions from Rice Straw Burning	11
2-1-5- Alternative Uses of Rice Straw	11
2-1-6- Cellulose, Hemicellulose and Lignin in Rice Straw	12
2-2-Cellulose	12
2-3-Hemicellulose	16
2-4- Lignin	17
2-5-Chemical Modifications of Cellulose	18
2-6-Dissolving Methods of Cellulose	20
2-6-1- Conventional Methods for Cellulose Dissolution	22
2-6-1-1- Viscose Process	23
2-6-1-2-Lyocell Process	25
2-6-2- Ionic Liquids	25
2-6-2-1-Ionic Liquids for Cellulose Dissolution and	28
Modification	
2-6-2-1-1- Ionic Liquid and Cellulose Dissolution	28

Title Pa	ge No.
2-6-2-1-2- Ionic Liquid as Media for Cellulose Modification	29
2-6-2-2-Dissolution Mechanism of Cellulose in Ionic	30
Liquids	
2-7-Applications of Cellulose	32
2-8-Cellulose Derivatives	34
2-8-1-Preparation of Cellulose Derivatives with ILs	35
2-8-1-1 Esterification of Cellulose	35
2-8-1-1-A- Acetylation of Cellulose	35
2-8-1-1-B- Acetylation of Cellulose with Carboxylic Acid	36
Derivatives	
2-8-1-1-C-Sulphation of Cellulose	37
2-8-1-2- Carbanilation of Cellulose	38
2-8-1-3 -Etherification of Cellulose	38
2-8-1-3-A-Carboxymethylation, -ethylation and -propylation	38
2-8-1-3-B-Tritylation	38
2-8-1-3-C-Cationic Functionalisation	38
2-9-Utilization of Some Cellulosic Derivatives	39
2-9-1-Pulping and Paper Making	39
2-9-2-Beating	42
2-9-3-Sheet Formation and Making	43
Chapter 3 Materials and Methods	
3-1-Preparation of raw material	44
3-1-1-Determination of moisture content	44
3-1-2-Ash content	45
3-1-3-Lignin content	45
3-1-4-Hollo-cellulose content	46
3-1-5-α-cellulose content	46

Title	Page No.
3-2-Treatment of raw material	
First step: pulping process (Delignification)	47
Second ste: Bleaching process	47
3-3-Preparation of cellulose derivatives	48
3-3-1-Dissolution of cellulose by IL	48
3-3-2-Preparation of methylcellulose (MC) (methylation)	48
3-3-3-Preparation of carboxymethylcellulose (CMC)	48
3-3-4-Preparation of hydrogel from cellulose derivatives	19
3-4-Paper sheet formation	
3-5-Absorption test	
3-6-Fourier Transform infra red analysis (FT-IR)	51
3-7-Scanning Electron Microscope (SEM)	
3-8- Methods to Measure the Optical Properties of Hand - made	
Paper Sheet	
3-8-1- Basis Weight	51
3-8-2- Thickness	52
3-8-3- Whiteness	52
3-8-4- Brightness	52
3-8-5- Opacity	53
3-9- Methods to Measure The Mechanical Properties of Hand	
made Paper Sheet	
3-9-1- Bursting Strength	53
3-9-2- Tearing Resistance	53
3-9-3- Tensile Strength	55
Chapter 4 Results & Discussion	
4-1-Raw Material Analysis	
4-2-Preparation of Pure Cellulose from Rs	

Title	Page No.
4-3-Dissolution of cellulose	61
4-4 - Preparation of Cellulose Derivatives	64
4-4-1- Preparation of Methylcellulose	66
4-4-2-Preparation of Carboxy Methylcellulose	61
4-3 -Preparation of Hand made-Paper Sheet	73
4-4-Addition of MC and CMC in Hand made Paper-sheet	73
4-4-5-Modification of MC to MC-hydrogel	76
4-4-6-Modification of CMC into CMC –hydrogel	78
4-4-7-Addition of MC-hydrogel and CMC-hydrogel to Hand-	
made Paper- sheets	
Chapter 5 Discussion	
5-1- Preparation of Pure Cellulose From Rice Straw	90
5-2- Using Ionic Liquid to Dissolve Cellulose	91
5-3- Preparation of Cellulose Derivatives	93
5-4-Modification of MC and CMC to Their Hydrogels	95
5-5-Addition of MC-hydrogel and CMC-hydrogel to Hand-made	de 98
Paper-sheets	
Chapter 6	
Summary	101
Recommendations	104
References	105
Arabic Summary	122

List of Figures

Fig. No.	Title	Page No.
1	Rice straw in Egypt, ready for transport	7
2	Burning Rice Straw in Egypt	10
3	Fringed fibril model of the supramolecular structure of cellulose	13
4	The arrangement of cellulose and other polysaccharides in a plant cell wall. A section of the cell wall in a plant cell.	15
5	The molecular structure of cellulose	16
6	Monomers of Lignin	18
7	Strand of cellulose showing the hydrogen bonds within and between cellulose molecules	18
8	Structure of wood fiber	19
9	Chemical representation of two industrially important cellulose technologies (a) Viscose and (b) Lyocell processes	23
10	Imidazolium as cationic IL	26
11	Simplified scheme of the direct dissolution and subsequent precipitation of cellulose in a closed-loop process	29
12	The possible materials and technologies generated from cellulose dissolved in ILs	30
13	Functionalization routes for cellulose in ILs medium	32
14	Pulping and Paper Making	40
15	FT-IR for Rice straw-pulp	59
16	SEM for Rice Straw Pulp	60

Fig. No.	Title	Page No.
17	Scheme for the derivatization of cellulose in an ionic liquid including product isolation and solvent recycling	63
18	FT-IR of IL 1-Butyl-3 methylimidazolium chloride	65
19	SEM shows the structure of methylcellulose	69
20	FT-IR of methylcellulose	70
21	FT-IR of Carboxymethylcellulose	71
22	SEM of Carboxymethylcellulose	72
(23a)	SEM of the surface of the membrane of methylcellulose - hydrogel	81
(23 b)	SEM of the cross section of membrane of methylcellulose-hydrogel	82
(23c)	SEM of the swelling membrane (400%) of methylcellulose-hydrogel	83
(23d)	SEM for dry membrane of methylcellulose - hydrogel	84
24	FT-IR of methylcellulose - hydrogel	85
25	FT-IR of carboxymethylcellulose -hydrogel	86
(25a)	SEM for dry membrane of carboxymethylcellulose- hydrogel	87
(25b)	SEM of the surface of the membrane of carboxymethylcellulose- hydroge	88
(25c)	SEM of the swelling membrane (583%) of carboxymethylcellulose- hydrogel	89

List of Tables

Table No.	Title	Page No.
1	Commercially important cellulose esters and ethers	34
2	Characterization of Raw Material (Rice Straw).	57
3	Characterization of Rice Straw pulp.	58
4	Characterization of bleached Rice Straw.	58
5	Optical properties of hand-made paper sheet with MC.	74
6	Mechanical properties of the hand-made paper sheet with MC.	74
7	Optical properties of the Hand made paper sheets with CMC.	75
8	Mechanical properties of the Hand made paper sheets with CMC.	76

List of Abbreviations

AGU anhydro glucose unit

BC bacterial cellulose

CMC Carboxy methyl cellulose

DP Degree of polymerization

DS degree of substitutions

FT-IR Fourier Transform infra red analysis

HEC Hydroxy ethyl cellulose

IL Ionic liquid

MC Methyl cellulose

MCC microcrystalline cellulose

OD oven dried

Rs rice straw

SEM Scanning Electron Microscope

TAPPI OM Technical Association of the Pulp and Paper Industry -

Official Method

t/a ton /annum

t/ha ton /hectar

UV Ultra violet

V volume

W weight

 Δ heat

List of Symbols

(AMIM)Cl: 1-ally-3-methylimidazolium chloride (BMIM)Cl: 1-butyl-3-methylidazolium chloride

(C₆H₁₀O₅) _X: CELLULOSE unit CDI: N,N'-carbonyldiimidazole

CH₃: methyl

C1: Chloride anions

CO2: CARBON DIOXIDE

CS₂: Carbon disulfide

Cu(NH₃)₄(OH)₂: copper ammonia solution

Cu (en) (OH)₂: copper ethylene diamine solution

DMSO: dimethylsulfoxide DMF: dimethylformamide

DMA/LiCl: N,N-dimethylacetamide/lithium chloride

(EMIM): 1-Ethyl-3-methylimidazolium cation

[Emim] Cl 1-ethyl-3-methylimidazolium chloride

EMIM dicyanamide (C_2H_5) (CH_3) C_3 H_3 $N_2^+N(CN)_2^-$

H₂SO₄: Sulfuric acid

H₂O: water

H₂S: hydrogen sulfide

K Br: potassium bromide

KOH: POTASIUM HYDROXIDE

KPS: potassium per sulfate

Na⁺: Sodium cations

Na Cl: Sodium chloride

NaOH: SODIUM HYDROXIDE

NH₄Br: Ammonium bromide

NMMO: N-methylmorpholine - N - oxide

-OH: hydroxyl groups PF: paraformaldehyde

THF: tetrahydrofuran